SOME REACTIONS OF FLUOROCARBON NITRILES: SYNTHESES OF AMIDINES, THIOAMIDES AND TRIAZINES

By

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PRELIMINARY REMARKS

All temperatures reported in this dissertation are in the centigrade scale and uncorrected.

Refractive indices were determined with a Abbe' Refractometer at 25°.

Molar refractions were calculated by the Lorenz-Lorentz Equation.

$$MR_D = \frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$$

The value for the atomic refractions were taken from Lange's Handbook, Eighth Edition. A value of 1.100 was used for fluorine.

Densities were determined at 25° with a pycnometer calibrated with water @ 25°.

Molecular weights were determined by the method of Vapor Density employing the method of Victor Meyer.

INTRODUCTION

The discovery that fluorine could be combined with carbon to produce a new series of compounds furnished the beginning for the development of a branch of chemistry known as fluorocarbon chemistry. The impetus for the rapid development of this field was provided by the fact that the compounds formed of the union of fluorine and carbon produced some of the most chemically inert materials known to man. The latter day development of the field however, is due to the discovery of the more reactive fluorocarbon derivatives and their employment in chemical synthesis. The scope and usefulness of the compounds so produced have made the field of fluorocarbon chemistry one of the most intensively studied branches of chemistry today.

The research that has followed the discovery of these compounds has shown that the reactions of fluorocarbon derivatives are not identical with analogous organic reactions but extend from modified organic reactions to some reactions not found in organic chemistry. This variation in reactivity from conventional organic reactions has provided the chemist with many unique and interesting compounds.

On the basis of our present day knowledge of carbon

fluorine compounds and their derivatives, it would appear that almost any hydrocarbon compound structure can be produced in the fluorocarbon series and some not found in organic chemistry. In the cases where this has been accomplished, the replacement of the hydrocarbon structure in the molecule by the fluorocarbon structure has been found to produce compounds whose properties and reactivity are to a great extent altered or even completely changed. The next step then is to employ these molecules in chemical synthesis.

One area of the field of fluorocarbon chemistry which shows promise of being of great importance is that of nitrogen containing fluorocarbons. In the field of organic chemistry, the nitrogen derivatives of hydrocarbon compounds occupy a position significant in importance and development. The field of the nitrogen containing fluorocarbon derivatives shows much promise but has been investigated only to a very limited extent.

One specific area of the field of nitrogen derivatives which should produce some interesting reactions and compounds is that of the nitriles or cyanides. The nitrile group, being of an unsaturated character, is highly reactive. This unsaturation of the carbon to nitrogen bond combined with the strong electronegative effect of the fluorocarbon radical should show enhanced reactivity or reactivity of a nature sufficiently different to produce a significant change in the final products of the reactions.

It has been noted that many of the reactions of nitriles require acid catalysts to initiate the reaction and in many cases

the initiating acid is necessary to stabilize the products. Thus, the ammonolysis[34] of organic cyanides occurs generally in the presence of the hydrochloride of the amine. Alcoholysis[35] and reactions with mercaptans[36] involve an activated nitrile nucleus, and product stability is only accomplished through salt formation. It has been noted by Kindler and Treu[24] while studying the influence of substituents on aromatic nitriles, that the more electron inducing the attached group, the greater was the reactivity of the nitrile toward hydrogen sulfide addition. Polymerization studies of nitriles[17] indicate that once again acid was necessary to initiate the polymerization, indicating that a more reactive center than that presented by the free organic nitrile is necessary for reactivity.

The reactive nitrile structure may be presented as:

$$R\text{---}C\equiv N$$

δ = partial charge

The fact that acid catalysis is so effective in addition reactions and polymerizations is probably due to the fact that the proton stabilizes and enhances the reactive carbon site so that under acid catalysis the reactive molecule now appears as:[1]

$$R\text{-}C=NH$$

This structure now provides a cationoid site very suitable for reaction. The alkforylnitriles would have an additional advantage in that the inductive effect of the very electronegative fluorocarbon radical will

activate the molecule to such an extent that any acid catalysis would be unnecessary.

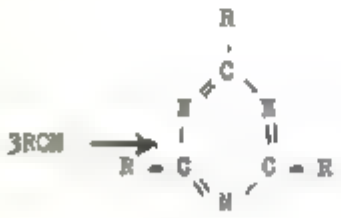
This contention was found to be true in that what would be considered abnormal reactions among hydrocarbon compounds were found to be quite normal reactions for alkfurylnitriles.

This can be shown by considering some reactions of organic chemistry and comparing them with what might occur in the fluorocarbon nitriles.

Oxley, Partridge and Short[34] have shown in the reaction of amines with cyanides to form amidines, that an equilibrium mixture is established, and through the choice of suitable conditions, amidines could easily be produced. Since amidines are usually stronger bases than the amines or ammonia from which they are produced, carrying out the reaction in the presence of an ammonium salt produces an amidinium salt. Provided the temperature was below the dissociation temperature for the salt, the equilibrium would be disturbed and the conversion of the cyanide into the amidine would be promoted. The reaction appears to be controlled by a number of factors. The presence of a more strongly anionoid nitrogen atom in the base would facilitate addition to the cyanide, the increase in strength of the base would decrease the proportion of the amidine converted to salt with a corresponding smaller displacement of the equilibrium between the cyanide, base and amidines.

The use of alkfarylnitriles in these experiments should eliminate both of these complications. The enhanced reactivity of the cyanide group due to the inductive effect of the fluorocarbon radical to which it is attached, would cause the base to be attracted to the cationoid site more easily. Once the amidines are formed, even though the fluorocarbon radical would tend to decrease its basicity, the amidine would not be affected by any equilibrium or competition with the base for the available acid to stabilize itself. This stability should be an inherent property of the molecule itself. Therefore, alkfarylnitriles should have at least two advantages over organic nitriles in ammonolysis. The first is a more readily available reaction site and the second is the fact that no imparted stimulus is necessary to stabilize the molecule, once it is formed.

Another phase of the reaction of nitriles that would appear to be of interest is that of polymerization of these compounds. In the field of organic chemistry, nitriles are known to trimerize to form the cyanuric ring:

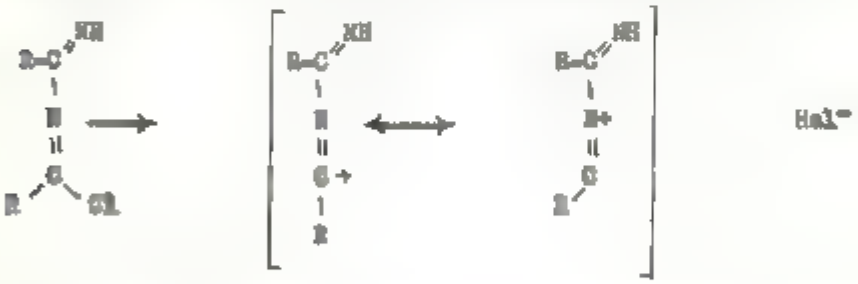


Benzonitrile was found by Gloss[17] to condense under the influence of sulfuric acid to form cyaphenin. There are many additional references to the polymerization of individual nitriles.[19, 48] Muñoz, Pierce and Belt[30] polymerized trichloroacetonitrile under the influence of hydrogen

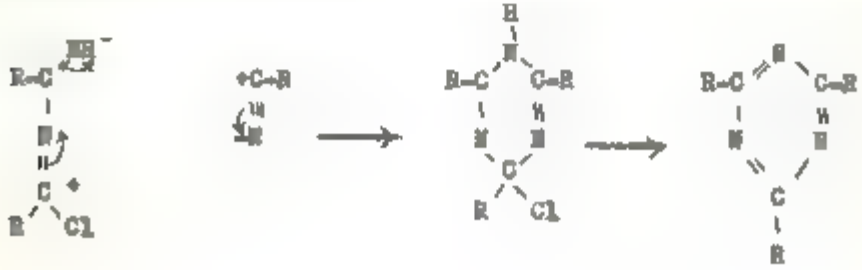
chloride and pressure to produce the 2, 4, 6 tris (trichloromethyl) 1, 3, 5 triazine, which they then fluorinated to give the alkoryl derivative along with eight other fluorine containing compounds. The substance was found to be very resistant to acid and exhibited no basic properties at all.

The effect of the fluorocarbon group in these polymerization reactions would appear to be interesting and worthy of study. The expected activation of the nitrile should occur and polymerization should then be of an uncatalyzed nature.

Grundmann, Weisse, and Seide[16] have proposed an interesting mechanism for triazine formation in an acid catalyzed state. The "primary product" is a substituted imino chloride of the type



It is a salt like structure which on decomposition with water yields the secondary amide. They propose the next step to be a diene synthesis type reaction in which the "primary product" is the diene and the third mole of nitrile is the dienophile.



The product then loses hydrogen chloride and aromatizes to form the triazine. The same thing could happen with the activated alkfaryl nitrile molecule to give a similar diene arrangement followed by coupling to give the triazine.

These then were some of the interesting possibilities that presented themselves when the work was undertaken. The intent of the work was to study the effect of the adjacent fluorocarbon radical on a reacting nitrile site with expectation of chemically establishing some preconceived ideas as to the nature of the reaction of alkfarylnitriles in addition reactions. The work was further extended to use the alkfarylamidines produced as a synthetic tool in preparing other fluorocarbon derivatives.

History

The history of fluorocarbon compounds and their derivatives must date back to the discovery of fluorine by Moissan in 1886.[29] Progress was very slow at the start, due partly to the experimental difficulty in preparing fluorine and the extraordinary reactivity of the element, causing it to react explosively with most organic compounds. Probably the first fluorocarbon produced was methforane as prepared by Lebeau and Damiens in 1926.[26] It was prepared by the action of fluorine on charcoal. Ruff[40] followed up this work and fully characterized the compound methforane, along with some observations on higher homologs, possibly ethforane and propforane, also produced in the reaction. Later, Simons and Block,[44] employing mercury salts as an explosion inhibitor, reported a direct fluorination of carbon and isolated a number

of fluorocarbons. With the elucidation of the physical properties and the chemical inertness of these compounds which occurred as an homologous series analogous to hydrocarbons, it was soon that these compounds might well serve as a basis for a new chemistry founded on fluorocarbons rather than hydrocarbons.

The interest in these new compounds soon provided new ways of preparing fluorocarbons. These consisted of (1) controlled reaction between elementary fluorine and liquid hydrocarbons, copper mesh being employed to provide effective geometry for reaction,[44,14,28,49] silver plating of the copper gauze to provide catalytic surface as well as beneficial geometry;[15] (2) powerful fluorinating agents such as cobaltic fluoride which were prepared [6, 38] and used in the replacement of chlorine by fluorine to produce a fluorocarbon,[40, 12] and (3) probably the most versatile and most commercially applicable process was the electrochemical process as reported by Simons.[45] This last process involved the production of fluorocarbons and fluorocarbon derivatives from carbon containing materials by the passage of an electric current of low voltage through a mixture of hydrogen fluoride and the carbon containing compound. A great number of materials could be employed such as hydrocarbons, carboxylic acids, esters, alcohols, acid chlorides, ethers, amines, sulfides, etc., giving the chemist a wide variety of starting materials with which to work. It was these latter day developments which paved the way for the tremendous volume of synthetic endeavor now being done in this new and rapidly expanding field of chemical research.

Reactions of Fluorocarbon Nitriles

Acetfluoronitrile* was first prepared by Swarts[47] in 1922. It was prepared by the dehydration of the acetfluoramide through the action of phosphorus pentoxide. Since that time the other members of the series have been prepared in exactly the same fashion. The fluorocarbon nitriles undergo many of the reactions found among the organic nitriles. The fluorocarbon nitriles hydrolyse readily in base to form the acid salt and the ammonia. Hydrogenation over platinum oxide yields good conversion to the amine[26] and they undergo reaction with Grignard reagents to form alkfuryl substituted acetophenones.[22] The fluorocarbon nitriles have also been used with the Grignard reagent to produce a series of alkfuryl ketones.[31]

The most striking difference displayed by the fluorocarbon derivatives when contrasted with their organic analogs is in the boiling points of the two materials. The acetfluoronitrile boils about 145° below that of the hydrocarbon analog.[46]

The fluorocarbon nitriles are generally prepared from the amide, which is readily prepared from the ester or the acyl halide by ammonolysis and can be almost quantitatively dehydrated to the nitrile through the action of phosphorus pentoxide.[47] They can also be prepared by the electrochemical process, using the hydrocarbon analogs as starting materials. Fluorocarbon nitriles are produced although there is some decomposition to NF_3.

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*The nomenclature used throughout the text is that proposed by Dr. J. H. Simons. The reader is referred to Chem. Eng. News 26, 1317 (1948), for a more complete treatment of the subject.

[redacted]

[redacted]

The reactions and preparations which follow all have a common chemical source, namely the fluorocarbon nitrile. It would therefore be of some interest to list some general considerations of the reagents used and the methods of preparation for the starting materials used.

[redacted]

[redacted]	Purchased from Minnesota Mining and Manufacturing Company.
Propforic Acid	Purchased from Minnesota Mining and Manufacturing Company.
Butforic Acid	Purchased from Minnesota Mining and Manufacturing Company.
Anhydrous Ammonia	Purchased from the E. I. duPont de Nemours and Company., Inc.
Anhydrous Methyl Amine	Purchased from The Matheson Company, Inc.
Anhydrous Dimethyl Amine	Purchased from The Matheson Company, Inc.
Anhydrous Hydrogen Sulfide	Purchased from The Matheson Company, Inc.

The fluorocarbon nitriles were prepared as described in the literature with only slight modifications in the procedure.[47] The fluorocarbon nitriles as prepared were found after a one plate distillation to be of sufficient purity to use in these experiments. All major

purification was accomplished with the easily distillable ester or the equally easy recrystallizable amide since both of these products are quite stable and convenient to handle.

The preparation of the nitrile can be schematically represented by the following set of chemical equations:

$$R_fCOOH + ROH \xrightarrow{H_2SO_4} R_fCOOR + H_2O$$

$$R_fCOOR + NH_3 \xrightarrow{Et_2O} R_fCONH_2 + ROH$$

$$R_fCONH + P_2O_5 \longrightarrow R_fCN + H_3PO_4$$

$$R = CF_3-,\ C_2F_5-,\ C_3F_7-$$

The experimental method for the acetfluoronitrile will be described. The other members of the series were prepared by an analogous series of reactions.

Acetfluoronitrile

Ethyl acetfluorate.- Into a 500 cc round bottom flask, fitted with a reflux condenser and protected from atmospheric moisture by a drying tube, was placed 114 g. (1.0 mole) of acetfluoric acid. To this was added an ice cold mixture of 96 g. (2.0 mole) of ethyl alcohol and 75 g. (0.8 mole) of concentrated sulfuric acid. The mixture was allowed to stand at room temperature for two hours and then refluxed for an additional two hours. On cooling, the reflux condenser was removed and the flask fitted with a downward condenser. The crude product was obtained by stripping the reaction mixture of all liquid boiling below 70°. This crude ester was washed twice with saturated sodium carbonate solution and dried over

anhydrous calcium sulfate. The crude ester was fractionated in a distillation column packed with glass helices of approximately nine theoretical plates. The yield of pure ester boiling at 60-62° was 145 g. Yield 92%, based on amount of acid used.

Acetforamide.- A three necked 500 cc round bottom flask, immersed in a Dry Ice-acetone mixture, was fitted with a delivery tube and a condenser through which moist air was excluded by a calcium chloride drying tube. Into the flask was placed 158 g. (1.0 mole) of ethyl acetforate along with 100 cc of ethyl ether. Into this mixture was condensed a large excess of anhydrous ammonia. The reaction mixture was then allowed to warm up to room temperature and the excess ammonia allowed to distill off. The solvent was then stripped from the reaction mixture, leaving a white solid which could be recrystallized from ethyl ether-petroleum ether to yield pure acetforamide (m.p. 75°). The solid weighed 102 g., 91% of theoretical yield, based on the original amount of ester.

Acetforonitrile.- A mixture of 113 g. (1.0 mole) of acetforamide and 150 g. (1.1 mole) of phosphorus pentoxide was placed in a round bottom flask fitted with a reflux condenser which in turn was connected by a rubber tube to a glass trap immersed in Dry Ice-acetone mixture. The solid mixture, when heated to 150° and held at this temperature for three hours, evolved acetforonitrile which was collected in the trap. Distillation to a new trap produced 76 g. of acetforonitrile. Yield 68% of theoretical based on the amide used.

Amidines

Fluorocarbon Amidines

Acetfluoramidine.- A reaction vessel consisting of an 80 ml. cylindrical glass flask, fitted with a delivery tube and connected to a Dry Ice-acetone reflux condenser, was placed in a Dry Ice-acetone bath. Into the flask was distilled 11.2 g. (0.10 mole) of acetfluoronitrile. A large excess of anhydrous ammonia was then allowed to condense into the reaction vessel containing the condensed nitrile. The Dry Ice-acetone bath was removed and the mixture allowed to reflux under the Dry Ice-acetone condenser for one hour. It was noted that the mixture did not react at Dry Ice-acetone temperature, but at slightly above this temperature a violent reaction ensued. The excess ammonia was allowed to distill off and the reaction mixture allowed to come to room temperature. The resulting product was then fractionated through a column packed with glass helices under reduced pressure to free it of any dissolved ammonia. The final product was a colorless liquid, b.p. 35-36° @ 11 mm. n_d^{25} 1.3801, d^{25} 1.4960.

Analysis Calculated for $C_2F_3N_2H_3$: N, 25.00% Found: N, 24.84%

The succeeding members of the series were low melting solids which resulted when the excess ammonia was allowed to distill off from the reaction mixture. These were recrystallized from ethyl ether-petroleum ether in the cold to remove any dissolved ammonia and when dried they were not found to be hygroscopic. A summary of properties

follows in Table I.*

Analysis - Kjeldahl's Method: Sample refluxed with concentrated sulfuric acid and Selenium metal; steam distilled into an excess of standard acid and back titrated with base to methyl red end point.

Properties - The amidines are slightly basic compounds, soluble in ether, alcohol and acetone, but insoluble in water. They hydrolyse in aqueous inorganic acid to form the ammonium salt of the inorganic acid and fluorocarbon acid. They hydrolyse in aqueous or alcoholic base to form the fluorocarbon amide or acid and ammonia. The amidines were not found to be hydroscopic if properly freed of ammonia.

N-methyl and N, N-dimethyl Alkfoxyl Amidines

N-methyl Acetformamidine.- A reaction vessel consisting of an 80 ml. cylindrical glass flask fitted with a delivery tube and connected to a Dry Ice-acetone reflux condenser was placed in a Dry Ice-acetone bath. Into the reaction vessel was condensed 11.2 g. (0.1 mole) of acetformnitrile. To the condensed nitrile was added a moderate excess 6.2 g. (0.2 mole), of methyl amine. The Dry Ice-acetone bath was removed and the mixture allowed to reflux under the Dry-Ice acetone condenser for one hour. At the end of this time the excess amine was allowed to distill off, leaving behind a high boiling liquid. The liquid was

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*It has been called to the attention of the author that these compounds have been reported in a patent[19] by a modification of the above procedure after the work had been completed in this laboratory.

TABLE I

Alkfuryl Amidines

$R_fC(NH)NH_2$ R_f	B.p., °C.	M.p., °C.	n_d^{25}	d^{25}	M. R. Calculated	M. R. Found	% N Calculated	% N Found	% Yield
CF_3-	35°-36° @ 11mm	-	1.3801	1.4960	17.58	17.50	25.00	24.84	90
C_2F_5-	-	48.5	-	-	-	-	17.21	16.93	95
C_3F_7-	-	52-53	-	-	-	-	13.22	13.21	75

distilled under reduced pressure to yield 14 g. of pure N-methyl perfluoroacetamidine b.p. 35-36° @ 11 mm, n_d^{25} 1.3801, d^{25} 1.4940. Analysis Calculated for $C_3F_3H_5N_2$ N, 22.20, M.R. 17.50. Found. N,21.85, M.R. 17.59.

The other members of the series were prepared in exactly the same manner. They were found to be more heat stable and did not require vacuum distillation. The distillation was through a nine plate column packed with glass helices. The analyses were as described for the unsubstituted amidines.

A list of the physical properties of the substituted amidines prepared appears in Table II.

Metal Salts of Alkforylamidines

Silver Salt of Acetforamidine.- To 5 g. (0.044 mole) of acetforamidine dissolved in 15 cc of anhydrous ethyl ether was added portionwise 4.60 g. (0.020 mole) of silver oxide. An immediate evolution of heat was noted along with the formation of a white solid. The mixture was vigorously stirred and any lumps of silver oxide noted were broken up. After all the black silver oxide was consumed, the white solid was filtered, washed a number of times with ethyl ether and then air dried. The material was found to be the silver derivative of the amidine. The salt decomposed on heating at about 200°C.
Analysis Calculated for $C_2F_3H_2N_2Ag$: N, 12.71, Ag, 48.78. Found: N, 12.28, Ag, 48.60.

The remaining members of the series were prepared in exactly the same manner. The silver salts were all found to be white solids, decomposing without melting at temperatures of 200° or above.

TABLE II

N-substituted Alkfory1amidines

		B.P.s °C.	d^{25}	n^{25}	% N Calcd.	% N Found	M. R. Obs.	M. R. Found
$CF_3C(NH)N(R')R$	R=H R'=Me	47-48° @ 21mm	1.2909	1.3919	22.20	21.85	23.59	24.10
	R=Me R'=Me	92°	1.1795	1.3812	20.01	19.72	29.10	27.40
$CF_3CF_2C(NH)N(R')R$	R=H R'=Me	126.5°	1.4258	1.3664	15.91	15.63	28.79	28.10
	R=H R'=Me	110°	1.2969	1.3678	14.75	14.43	33.79	33.20
$CF_3CF_2CF_2C(NH)N(R')R$	R=H R'=Me	137°	1.5140	1.3561	12.37	12.02	33.40	32.50
	R=Me R'=Me	120°	1.4242	1.3548	11.66	11.41	38.38	36.70

The properties of silver salts of alkforylamidines are given in Table XII.

Mercury Salts of the Butforamidine.- In a test tube immersed in an oil bath was placed an intimate mixture of 10 g. (0.046 mole) of butforamidine and 5 g. (0.023 mole) of mercuric oxide. The mixture was heated to 110° to melt the amidine and was vigorously stirred. The formation of the white mercury salt could be noted and was essentially complete in two hours. The melt was allowed to cool and unreacted amidine was leached out of the solid by continuous extraction of the solidified melt with ethyl ether. The unreacted mercuric oxide could be removed by centrifugation using ethyl ether as the solvent. The heavier mercuric oxide settled first and the upper layers were found to be essentially the amidine mercury salt. After a number of centrifugations, the pure salt was obtained as a white solid that decomposed at 176°. Analysis Calculated for $C_6F_{13}N_3H_2Hg$: N, 9.00, Hg, 32.31. Found: N, 8.42, Hg, 32.60.

The mercury salt of the acetforamidine could not be prepared since this amidine decomposed very easily when heated. The propforamidine reacted in exactly the same fashion as the butforamidine to give a mercury derivative.

The properties of the mercury salts of the alkforyl amidines are summarized in Table IV.

Attempted Preparation of the Alkali Metal Salts of the Alkforyl Amidines

Potassium Amide and Butforamidine in Liquid Ammonia.- Potassium amide was prepared by dissolving potassium metal in liquid ammonia using

TABLE III

N-Silver Alkfloryl Amidines

$R_fC(NH)NHAg$ R_f	M.p., (dec.) °C.	% Ag Calculated	% Ag Found	% N Calculated	% N Found
CF_3-	200 (dec.)	48.78	48.40	12.71	12.28
C_2F_5-	240 (dec.)	40.02	40.38	10.36	10.27
C_3F_7-	277 (dec.)	33.60	32.80	8.74	8.50

TABLE IV

N-Mercury Alkfuryl Anilines

$(R_fC(NH)NH)_2Hg$ R_f	M.P., (dec.) °C.	% Hg		% N	
		Calculated	Found	Calculated	Found
C_2F_5-	159 (dec.)	38.38	38.20	10.65	10.22
C_3F_7-	178 (dec.)	32.31	32.60	9.00	8.42

iron as a catalyst.

In a flask containing 5 g. (0.10 mole) of potassium amide and 17 g. (1.0 mole) of liquid ammonia was added 21 g. (0.10 mole) of butformamidine. The mixture was allowed to reflux under a Dry Ice-acetone condenser for one hour. On removal of the excess ammonia a viscous orange syrup remained. The viscous syrup appeared to be hydrocuspin and on distillation was found to decompose.

Potassium amide and the butforyl nitrile in liquid ammonia.- To a flask containing 5 g. (0.10 mole) of potassium amide was condensed 19.5 g. (0.10 mole) of butforyl nitrile. A large excess of ammonia was condensed in with the mixture and the contents of the flask were allowed to reflux under a Dry Ice-acetone condenser for one hour. The solution gradually darkened to a deep brown. The excess ammonia was allowed to distill off leaving a brown syrup from which nothing could be distilled or extracted.

Potassium hydroxide and butformamidine in methyl alcohol.- In a flask containing a solution of 5 g. (0.10 mole) of potassium hydroxide dissolved in 25 ml of methanol was added 21 g. (0.10 mole) of butyramidine. The mixture was allowed to stand one hour. The alcohol was removed leaving a heavy syrup from which only butformamide could be distilled. The rest of the material resisted both extraction and distillation.

Acid Salts of Alkforyl Amidines

The acetforic acid salt of butyramidine.- In a round bottom flask containing 15 cc of acetforic acid was dissolved 5.3 g. (0.085 mole)

of butforamidine. The clear solution which formed was allowed to stand for one hour. The excess acid was removed under reduced pressure leaving a residue consisting of a white solid. The solid residue could be purified by sublimation and was found to be the acetforic acid salt of the butforamidine.

Analysis Calculated for $C_6F_{10}N_2O_2H_2$ N, 8.59; M.W., 326. Found: N, 8.44; M.W., 324.

The alkforyl amidines were found to form salts with inorganic, organic and fluorocarbon acid. The procedures were the same for all the salts except in the case of the formation of the alkforyl amidine hydrochloride. Formation of the amidine hydrochloride necessitated dissolving the amidine in anhydrous ethyl ether and bubbling anhydrous hydrogen chloride through the solution from which the fluorocarbon amidine hydrochloride separated. Some representative acid salts are given in Table V.

Acylated Alkforyl Amidines

N-Benzoyl butforamidine.- A solution of 24.6 g. (0.174 mole) of benzoyl chloride was placed in a round bottom flask fitted with a dropping funnel, condenser and protected from atmospheric moisture by drying tubes. The flask was cooled in an ice bath until the contents were at 0°. A solution of 57 g. (0.174 mole) of butforamidine in 50 cc of dry ethyl ether was slowly added to the flask. An immediate evolution of hydrogen chloride was noted along with a white precipitate of the butforamidine hydrochloride. After the addition was complete, the flask was allowed to warm up to room temperature and to stand for one

TABLE V

Acid Derivatives of Alkfoxyl Amidines

	M.P., °C.	M. E. Calculated	M. E. Found	% N Calculated	% N Found
$CF_3C(NH)NH_2.HCl$	>360	149	143	-	-
$CF_3C(NH)NH_2.CH_3COOH$	Subl.	172	174	16.29	15.94
$CF_3C(NH)NH_2.C_3F_7COOH$	Subl.	326	323	8.58	8.80
$C_3F_7C(NH)NH_2.HCl$	130°	249	241	-	-
$C_3F_7C(NH)NH_2.CH_3COOH$	Subl.	272	277	10.20	10.26
$C_3F_7C(NH)NH_2.C_3F_7COOH$	Subl.	426	420	6.58	6.43

hour at this temperature. The mixture was filtered free of the white amidine hydrochloride and the ethereal solution carefully stoppered to preserve it from the atmosphere. The ethereal solution was found on dilution with petroleum ether and cooling to precipitate a solid melting at 61-63°C. Recrystallisation from ethyl ether-petroleum ether gave a white solid, mp. 63°C.

Analysis Calculated for $C_{11}F_7H_7ON_2$: N, 8.86; Found: N, 8.58

The acetyl derivative was prepared in the same manner and was found to be a liquid boiling at 152°. The great susceptibility of the derivative to hydrolysis may account for the poor nitrogen analysis.

Analysis Calculated for $C_6F_7H_5N_2O$: N, 11.06; Found: N, 10.37

Saponification equivalent: Calculated: 254; Found: 255

Butforyl chloride was found to react with the butforamidine to give a variety of products, none of which could positively be identified as the desired acylated derivative.

The reaction was carried out exactly as described for previous preparations, the following products being isolated and identified in the reaction mixture:

1. butforamidine hydrochloride
2. liquid fraction boiling at 73° @ 6½ mm gave neutral equivalent indicating it was butforic acid
3. liquid fraction boiling at 115-116° @ 6½ mm which hydrolised quite rapidly on standing, to give only butforamide.

The Butforamidine with Sodium Hypobromite

A 500 cc round bottom three necked flask containing 36 g. (0.90 mole) of sodium hydroxide dissolved in 100 cc of water was fitted with a stirrer, dropping funnel and condenser. The condenser was connected by a delivery tube to a trap cooled in Dry Ice-acetone mixture. The reaction vessel was cooled to 0°, 28.8 g. (0.18 mole) of bromine was added dropwise and cooling and stirring continued until the red color of bromine disappeared and only a light yellow color remained. To this solution was added 32 g. (0.150 mole) of butforamidine along with an additional 50 cc of water. The amidine slowly dissolved in the solution. The reaction mixture was left for one hour in the ice bath, allowed to come to room temperature and refluxed for two and one half hours at 100°C. The Dry Ice-acetone trap yielded after distillation through a packed column 2.6 g. of material boiling at 17-18° with molecular weight of 253, which could be identified as the propfuryl bromide. The contents of the flask on acidification yielded large amounts of the butforamide.

Fluorocarbon Thioamides

Thiobutforamide from butforonitrile.- Into a heavy walled pyrex glass tube of approximately 60 ml. capacity, previously constricted for sealing and evacuated, was allowed to condense 6.8 g. (0.35 moles) of butforonitrile and 3.4 g. (0.10 moles) of hydrogen sulfide. The tube was sealed off and allowed to warm up to room temperature and left at this temperature overnight. The tube was opened and the volatile material, consisting entirely of hydrogen sulfide, was allowed to

distill off into a vacuum system leaving behind 8 g. of a pale yellow solid. The solid was recrystallised from ether-petroleum ether, yielding 6.3 g. of pure thiobutforamide, m.p. 49°.
Analysis Calculated for C_5H_7NS: N, 6.12; S, 13.97 Found: N, 5.85; S, 13.81.

The thiopropforamide could be prepared in the same manner, the reaction proceeding at room temperature.

The thioacetforamide was not successfully prepared under these conditions, a considerable amount of charring taking place in the reaction vessel. It was found that if the reaction was kept at 0° for eighteen hours, satisfactory yields of the thioacetforamide were obtained. The reaction could also be moderated through the use of a solvent such as ethyl ether, but reaction times were extremely long, (100-125 hrs.).

Thiobutforamide from butforamidine.- In a round bottom flask fitted with a two hole rubber stopper carrying a delivery tube and a drying tube, was placed 15 g. (0.071 moles) of butforamidine dissolved in 25cc of ethyl ether. Into this solution was bubbled an excess of hydrogen sulfide until the solution was completely saturated. The solution was then allowed to stand one hour. The ether was removed under reduced pressure and a high boiling liquid was left in the flask. The liquid sometimes crystallised on standing to yield the crude thioamide. Usually the liquid was distilled under reduced pressure to produce a liquid which immediately crystallised on cooling. The product recrystallised from ether-petroleum ether was found to be yellow needles melting at 47-48°.

Analysis Calculated for $C_4F_7H_2NS$: N, 6.12; S, 13.97. Found: N, 6.01; S, 13.90.

This method was found to be quite suitable for the preparation of the other members of the series, yields being in most cases almost quantitative.

The properties of the fluorocarbon thioamides are summarized in Table VI.

2,4,6-tris(alkfloryl) 1,3,5, s-triazines

2,4,6-tris(ethfloryl) 1,3,5, s-triazine from propfluoronitrile.- Through the use of a vacuum system 54 g. (0.37 moles) of propfluoronitrile was condensed into a stainless steel autoclave. The autoclave was heated at 300° for 120 hours, after which the vessel was allowed to cool. The volatile material (27 g.) was allowed to distill out of the vessel before it was opened. The vessel was found to contain 16.8 g. of high boiling material. The high boiling material was subjected to distillation through a nine plate column giving 6.3 g. of colorless liquid boiling at 122-122.5°. n^{25} 1.3131. d^{25} 1.6506.

Analysis Calculated for $C_9F_{15}N_3$: N, 9.60; M.W. 435; S.E. 435. Found: N, 8.99; M.W. 431; S.E. 442.

The other fluorocarbon nitriles were found to act quite similarly to the propfluoronitrile with 300° as the optimum temperature for reaction. The butfluoronitrile however, gave better yields at the slightly higher temperature of 350°.

TABLE VI

Alkfoxyl Thioamides

$R_fC(S)NH_2$ R_f	B.p., °C.	M.p., °C.	% S Calculated	% S Found	% N Calculated	% N Found
$CF_3C(S)NH_2$	48° @ 2-3mm	-	24.78	25.13	10.82	10.85
$CF_3CF_2C(S)NH_2$	60° @ 23mm	39-40°	17.88	18.18	7.82	7.53
$CF_3CF_2OF_2C(S)NH_2$	69° @ 21mm	47-48°	13.97	13.90	6.12	6.01

2,4,6,tris(ethfoxyl) 1,3,5 s-triazine from propforamidine.- Into a round bottom flask fitted with a reflux condenser was placed 55 g. (0.34 moles) of propforamidine. The flask was placed in an oil bath and heated at 125° for three hours, the evolution of ammonia being noted. At the end of this time the resulting liquid was cooled and then subjected to distillation through a column packed with glass helices and calculated at nine theoretical plates. The distillate was a colorless liquid boiling at 122°, n^{25} 1.3135, d^{25} 1.0504.

The acetforamidine could not be used in this preparation since on heating, it produced a solid, a portion of which could be identified as the acetforamide. The butforamidine appeared to be a very suitable reagent in this reaction giving excellent yields of the butfoxyl substituted triazines.

The properties of the 2,4,6,tris(alkfoxyl) 1,3,5 s-triazines are summarized in Table VII.

Infrared Spectra of Alkfoxyl s-Triazines

A Perkins and Elmer Model 21 double beam infrared spectrophotometer was employed in the preparation of the spectrograms of the alkfoxyl s-triazines. A demountable cell consisting of two salt plates pressed over the liquid was used. The cell thickness was approximately 0.027 mm.

The infrared spectrograms for the alkfoxyl s-triazines prepared follow.

TABLE VII

Alkoxyl s-Trizines

R-C=N-C(R)=N-C(R)=N (R)	B.P., °C.	n^{25}	d^{25}	M.W. Calcd.	M.W. Found	S.E. Calcd.	S.E. Found	% N Calcd.	% N Found
CF_3	95-96°	1.3161	1.5930	285	[redacted]	-	-	-	-
CF_3CF_2	121-122°	1.3131	1.6506	435	431	435	442	9.60	8.99
$CF_3CF_2CF_2$	165°	1.3095	1.7158	-	-	576	585	7.18	6.96

% TRANSMISSION
100
0
15
14
9
7
5
3
μ

% TRANSMISSION
100
0
h
4
3
2
1
0
-1
-2
-3
-4

% TRANSMISSION
100
0
μm
15
12
10
9
8
7
6
5
4

DISCUSSION

Alkfaryl Amidines

The alkfaryl amidines were prepared by the action of anhydrous ammonia on fluorocarbon nitriles without the influence of acid catalysts. The conditions under which the alkfaryl amidines were prepared indicate that the formation of these compounds and the mechanism by which this reaction occurs are quite different from those found in organic chemistry. The fact that the fluorocarbon nitriles form stable free amidines by the addition of ammonia to nitriles is significant in that these molecules are the first easily prepared and stable examples of compounds of this type. There have been recorded two instances of amidines having been prepared[9, 11] by the addition of amines or ammonia to nitriles without acid catalysts. However, in one instance the isolation of the free amidine was claimed, but other investigators[34] could not obtain the compound except by formation of a picrate salt. In the other case, the material isolated was very unstable and had to be kept at very low temperatures under desiccation or else decomposition occurred. In both these instances the molecule to which ammonia was added was of an enhanced cationic type, the compounds being trichloromethyl cyanide and ethyl cyanotartronate. The enhanced reactivity of these compounds was probably due to the inductive effect of the substituents of the molecule. In this respect, these compounds show a similarity to the fluorocarbon nitriles

and probably reacted in a similar fashion.

The organic amidines have been prepared by a number of different methods, but there are only three of sufficient importance to be mentioned here; (1) the conversion of the imino ester to the amidine through the use of ammonia,[35] (2) the reaction of alkali metal amides with nitriles[8] and (3) the reaction of the acid salt of the amine or ammonia with the nitrile.[6] The last method is probably the most widely used preparation for the amidine. The methods of preparation can be summarized by the following chemical equations:

(1) $RCN + ROH \xrightarrow{HCl} RC(NH)OR \cdot HCl$

$RC(NH)OR \cdot HCl \xrightarrow{NH_3} RC(NH)NH_2 \cdot HCl + ROH$

(2) $RCN + NH_2 \xrightarrow{NH_3} RC(NH)NHK \xrightarrow{HCl} RC(NH)NH_2 \cdot HCl$

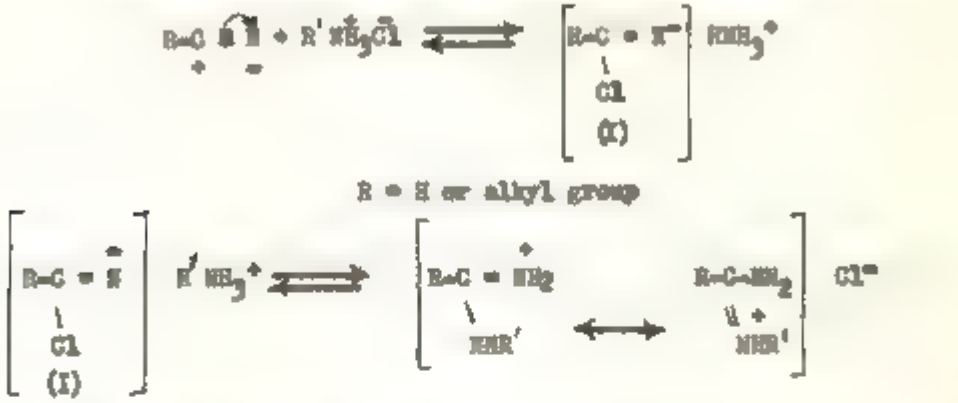
(3) $RCN + NH_4Cl \xrightarrow{NH_3} RC(NH)NH_2 \cdot HCl$

It can be seen from the description of the preparation of the amidine that the reaction is basically one of an anionoid agent (amine) seeking a cationoid site in the nitrile. The organic nitrile structure as we can construct it from our knowledge of its reactions is one in which there exist partial negative and positive charges in the molecule. This dipole arises in the molecules because of differences in electronegativity between the constituent atoms.[1] The organic nitrile may be pictured as:

$$R\text{-}C^{+\delta} \equiv N^{-\delta}$$

δ = partial charge

It has been suggested[33] that the formation of the amidine in the presence of amidic catalysts occurs according to the following mechanism:



R = H or alkyl group

The hypothetical intermediate (I) is unstable in the presence of the ammonium ion and probably through hydrogen bonding is decomposed by the ammonium ion to give the amidinium salt of the acid. This mechanism suggests that there are two conditions necessary for amidine formation among organic nitriles. The nitrile must be in an activated state having a suitable reaction site available and the amidine once formed must be more basic than the amine from which it was prepared. If the second condition was not met, the ammonia salt would preferentially remain and the equilibrium would shift to the side favoring ammonium salt and not the amidinium salt formation. A search of the literature on the basicity of organic amidines reveals that the value for only a single substance is available, namely acetamidine.[42] The value as given was pKb 1.59. Comparing this value with the pKb values for certain amines, it can be readily seen that the amidines are more basic than the ammonia compounds from which they are formed. It has been concluded by some investigators[33] that in general, amidine

formation is more complete with salts of weak bases.

[redacted]

Amine	pK_b^{25}
$(CH_3)_2NH$	3.29
CH_3NH_2	3.36
NH_3	4.74
$C_6H_5NH_2$	9.41

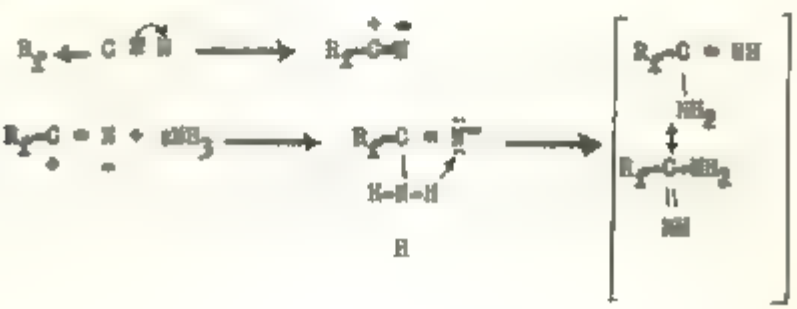
It has been noticed in the study of substituted benzamitrile that amidine formation is usually promoted by groups which act as electron sinks ($pNHSO_2$, Br, NO_2) and is retarded by those which act as electron sources (NH_2O, OH).[33] The inductive groups will aid in the formation of the complex by increasing the polarity of the molecule, but they also decrease the basicity of the amidine once it is formed. This will retard amidinium salt formation by displacing the equilibrium away from amidine formation.

The conditions under which the alkfaryl amidines form, indicate that neither of these two ideas postulated for organic amidine formation is of importance in the synthesis of alkfaryl amidines, since the path to formation appears to be quite different. Since no imported stimulus was necessary for alkfaryl amidine formation or stability, the difference between organic nitriles and the fluorocarbon nitriles must lie in the greater inductive effect of the fluorocarbon group adjacent to the nitrile structure. The electron withdrawing nature of the alkfaryl

group is known, as evidenced in studies in connection with the electrophillic addition to double bonds found adjacent to an alkfoxyl substituent.[46] The reactions of the fluorocarbon nitriles studied to date have in general been those of organic nitriles and have not shown a complete and clear picture of the possibilities of these fluorocarbon compounds. The value of the alkfoxyl radical adjacent to an unsaturated site becomes readily apparent in the reaction of the fluorocarbon nitriles to form amidines.

The fluorocarbon nitrile structure might be pictured as:

The inductive effect of the alkfoxyl group on one side of the reactive carbon site and the electronegative nitrogen atom on the other side impart an effect to this carbon center which renders it relatively positive. This cationoid site is present in the molecule without any outside stimulus. The ammonia molecule being nucleophillic in character is attracted to this positive site. The possible reaction mechanism may then be illustrated as:



It had been noted that when the reaction to form the amidine was conducted in the presence of ammonium chloride, no amidinium chloride was formed. This would indicate that the alkfoxyl amidine formed was a weaker base than the ammonia from which it was prepared. The postulate of an equilibrium between a hypothetical nitrile intermediate and the ammonium salt is not valid for the formation of the alkfoxyl amidine since the ammonium salt could be isolated readily from the reaction mixture. Although the alkfoxyl amidine was prepared in this reaction, no amidinium salt was found. This condition would have been impossible if a mechanism involving acid-catalysis was operating.

The mechanism then postulated for amidine formation from the fluorocarbon nitriles is the addition of ammonia to the free nitrile along with a proton shift to give the stable amidine.

N-substituted and NN-disubstituted Amidines

The substituted amidines can be looked upon as forming in the same manner as the unsubstituted amidines, the only difference being that the basicity of the amine appears to be very important for formation of the substituted amidine. The monosubstituted alkyl amine reacted quite readily as did the disubstituted alkyl amine; in both cases the reaction was as fast and as complete as with ammonia. It will be noted from Table VIII that the basicity of both of these amines exceeds that of ammonia. The fact that the phenyl substituted amines, such as aniline, would not react with the nitrile even after heating, could possibly be explained by the fact that the basicity of the amine

is an important consideration in the reaction. Aniline is a considerably weaker base than either ammonia or alkyl substituted amines and hence would yield a poor aminoid nitrogen to take part in the reaction. Additional study on the formation of amidines with respect to the strength of the base will be necessary before any more definite conclusions can be reached.

Amidinium Salts

The salts of the amidine show some very interesting properties with respect to the influence of the alkforyl radical on their acid-base strength. The organic amidines have been called by some investigators[13] carbonylic acids because of their acid like character in solution of anhydrous ammonia. It has been possible to produce metallic salts of the organic amidine using anhydrous ammonia as a solvent.[13] The organic amidine in solvents such as ether or water has been found to be too weak an acid for successful preparation of metallic derivatives. The fluorocarbon amidine, however, exhibits sufficient acid properties in organic solvents to form these metallic salts. This again indicates the electron inducing effect of the fluorocarbon group on the overall basicity of the amidine molecule. The silver and mercury salts of the amidines were prepared in anhydrous ether and were found to be crystalline materials which decomposed on heating. The salts which formed indicate that the alkforyl amidines are monobasic acids. Although three replaceable hydrogen atoms are available, only one hydrogen was replaced by the metallic ion. These structures may be represented by general formulas:

$$(R_fC(NH)NH)_xM$$

The alkali metal salts resisted all attempts at isolation and could not be prepared. A possible reason for this is the fact that when the reaction was run in aqueous or alcoholic media, hydrolysis occurred. When the alkfuryl amidine was treated with alkali metal in an anhydrous ammonia solvent decomposition occurred. The decomposition of fluorine containing compounds in liquid ammonia containing alkali metals has been noted by McBee[27] and has been used as a method of decomposition for analysis. The product of the reaction was a syrup which resisted crystallization, extraction or distillation. Since nothing that appeared to be of interest at the time could be isolated, the experiments were discontinued.

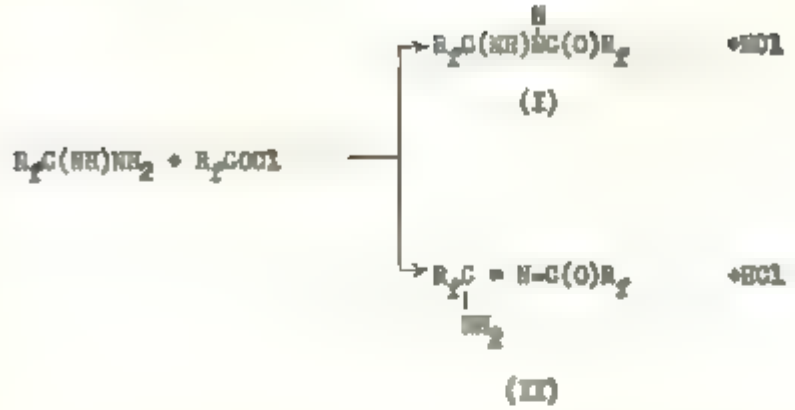
The alkfuryl amidines, besides being acid enough to form metal salts, exhibit basic properties in the same solvents which are sufficient to bring about the formation of acid salts. A number of these salts were prepared using inorganic, organic and fluorocarbon acids. Only one acid molecule reacted with one amidine molecule to form an amidinium salt. The structure of these compounds from analyses and neutral equivalents appears to be:

$$R_f\text{-}C(=NH_2^+)\text{-}NH_2 \cdot HA$$

Acylated Amidines

The alkfuryl amidines are quite easily acylated to form the N-substituted acyl derivatives. The course of the reaction leading to the N-acyl alkfuryl amidines could yield two tautomeric acylated

products.



The two isomeric forms should have distinctly different characteristics. Structure (I) should be acidic in nature due to the two adjacent electron inducing groups, while (II) should be a neutral molecule or at most a very weak acid. The hydrolysis of (I) should produce the mixed secondary amide (III) while hydrolysis of (II) would produce the primary amide (IV).

The N-benzoyl derivative of the butforamidine was found to be a neutral compound since it was not soluble in aqueous sodium hydroxide. The acetyl derivative was hydrolysed by aqueous base to form acetamide and the butforamide. The N-butforyl derivative which could not be obtained in a state sufficiently pure enough to characterise it, hydrolysed exclusively to the butforamide.

The sulphonic acid derivatives of the organic amidines have been shown to display a similar reaction.[2, 32] Thus, Barber using

sulfonyl derivatives ($R{-}SO_2{-}$) concluded that there possibly exists two isomers of these compounds, the stable form being of a structure similar to (I) and an unstable form similar to structure (II) which could be converted to (I). Northey[2] was able to isolate only one sulfonilyl derivative ($H_2N{-}C_6H_5{-}SO_2{-}$) which was incapable of forming the sodium salt and on hydrolysis gave amides of type (IV). The author concluded that a structure similar to (II) was more correct on the basis of the data obtained.

A comparison of the two structures of the acylated amidines will show that the existence of the two different compounds can be accomplished when an electron inducing substituent is adjacent to the amidine functional group. This electron inducing group can then serve to immobilize the hydrogen atom and prevent prototropy.

This type of tautomerism would occur but for the electron inducing effect of the alkoxyl radical which stabilizes the imino nitrogen so that the rapid exchange of proton is lessened or entirely halted.

A consideration of the hydrolysis products and the apparent neutrality of the acylated alkoxyl amidines would lead to the conclusion that the acyl derivatives of the alkoxyl amidines probably exist as structure (II).

Reaction of Butforamidine with Sodium Hypobromite

The reaction of the butforamidine in the presence of sodium hypohalite was found to produce the propforyl bromide and the butfor-

It has been shown by Hunted and Kohlhase[20] that the alkforyl amides give unexpected results in the Hoffmann Hypobromite Reaction, the butforamide forming propforyl bromide instead of the expected propforyl amine. This same product was obtained with the butforamidine. The reaction as applied to the butforamide was given as:

$$R_2C(O)NH_2 + NaOBr \longrightarrow R_2C(O)NHBr$$

$$R_2C(O)NHBr \xrightarrow{NaOH} R_2Br + CO_2 + NH_3$$

The N-bromo substituted amide being an isolatable compound.

The reaction mechanism for conversion of butforamidine to propforyl bromide indicates that the amidine was first hydrolyzed to the amide and that the latter then reacted with sodium hypohalite to give the isolated propforyl bromide.

All attempts to prepare an N-bromo substituted amidine were without success, the reaction being tried in a number of solvents under a variety of conditions. This indicates that under normal conditions of formation of N-bromo derivatives of the amidines the alkforyl amidines do not react to give these compounds. The silver salts of the alkforyl amidines were also used without any success. The mechanism then proposed for the formation of the propforyl bromide from the butforamidine, since the butforamide was isolated in the reaction mixture,

is for the formation of the butformamide by hydrolysis and then bromination followed by elimination and rearrangement.

Fluorocarbon Thioamides

The fluorocarbon thioamides were prepared by two different methods. The action of hydrogen sulfide was found to convert both the fluorocarbon nitriles and the fluorocarbon amidines to the fluorocarbon thioamides at room temperature.

The fluorocarbon nitrile when sealed in a glass tube with hydrogen sulfide was found to react at room temperature to produce the fluorocarbon thioamide. The reaction was found to be very rapid, and in the case of acetfluoronitrile so vigorous that charring of the reactants or products occurred.

The organic nitriles have been found to add hydrogen sulfide under the influence of heat and pressure[7, 5] the reaction being catalyzed by alkali hydrosulfides. It was shown that electron inducing groups aid in the addition of hydrogen sulfide to aromatic nitriles, the time for reaction decreasing with the more electronegative a substituent on the ring.[23] The rapid reaction of the fluorocarbon nitriles shows again the great electron affinity of the alkfoxyl radical, since these compounds form almost quantitative yields of the fluorocarbon thioamides by hydrogen sulfide addition at room temperature.

The fluorocarbon amidines react with hydrogen sulfide in a solvent of ethyl ether at room temperature to form the fluorocarbon thioamides. The reaction requires a large excess of hydrogen sulfide to convert the fluorocarbon amidines to the fluorocarbon thioamides.

The fluorocarbon thioamides prepared in this manner were found to be substantially pure since in most cases even before distillation they solidified. The fluorocarbon thioamides as prepared were found to be low melting, pale yellow solids with the exception of the first member thioacetfluoramide which was a pale yellow liquid. The thioamides appeared to be quite stable and could be stored for a number of weeks in sealed vials without any apparent decomposition.

Alkfluoryl Triazines

The preparation of the 2,4,6tris(alkfluoryl) 1,3,5 triazine was accomplished by two different methods. The first involved the trimerization of the alkfluoryl nitrile under pressure. The second concerned the coupling of three moles of alkfluoryl amidine with the resultant loss of ammonia to form the triazine.

Trimerization of the fluorocarbon nitriles under pressure.- The fluorocarbon nitrile was found to trimerize under the influence of pressure to form the triazine, no acid catalysis being necessary. There was no definite set of conditions for trimerization found, but the pressure range found most satisfactory was between 700-900 p.s.i. The optimum temperature appears to be between 300-350° and the reaction time may vary between 30-120 hours, the criteria being a sufficiently great pressure decrease.

The fluorocarbon nitriles show a striking difference in polymerization when compared with their organic analogs, in that no activating influence was necessary to effect this reaction. The mechanism proposed for the formation of a triazine under the influence

of acid has been a diene type synthesis in which two moles of the nitrile condense to form the diene and the third mole of the nitrile then acts as the dienophile. The mechanism appears to be applicable to the synthesis of the triazine from the alkfloryl nitrile. The reaction sequence is listed below.

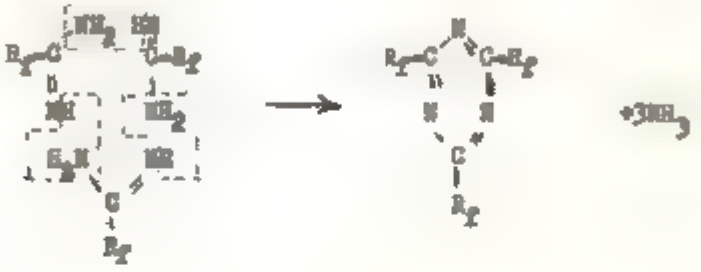
diene dienophile

A possible mechanism which is proposed is that two moles of the more active fluorocarbon could condense to form a diene type structure followed by condensation with a third mole to form the triazine.

The reaction appears to require rigid rules for the size of the molecule involved, for, as the size of the alkfloryl radical increased, the yield of the triazine was noted to decrease. The effects of pressure was noticed to have an effect upon the synthesis. At the lower pressures of 300-400 p.s.i., reaction did not take place, but at pressures over 600 p.s.i., effective trimerization was accomplished.

Condensation of the alkfloryl amidines.- The alkfloryl amidines when heated in the atmosphere above their melting points trimerize to form the alkfloryl s-triazine in good yield. The exception is the acetfloroamidine which was found to hydrolize in atmosphere on heating to form the corresponding amide. The reaction appears to be a coupling

of three moles of the amidine with splitting out of ammonia to form the triazine. It was found that when butforamidine was heated, just slightly less than the theoretical amount of ammonia was evolved for the coupling as described below.



The alkforyl triazines were found to be a neutral substance very resistant to acid attack. The 2,4,6,tris(propforyl) 1,3,5, s-triazine was stable to concentrated sulfuric acid even after 72 hours at 300°C. The triazines were found to be very susceptible to alkaline hydrolysis giving the sodium salt of the fluorocarbon acid on treatment with aqueous alkali and the esterified fluorocarbon acid on alkaline alcoholic hydrolysis.

The following charts are inserted for comparing the two methods devised for preparing the alkforyl s-triazines. In Table IX, the values for the temperature and the time are shown as those which gave the best yield of the alkforyl s-triazine in these experiments. The pressure is an autogenous pressure and depends upon the quantity of starting material employed; however, pressures above 600 p.s.i., were necessary for trimerization.

Table I gives the comparative yield of the two methods for the preparation of the alkforyl s-triazines:

Table IX

Optimum Conditions for Alkfoxyl Nitrile Trimerization

R	Temp. °C.	Time hrs.	Pressure p.s.i.	Yield %
CF_3-	300	28	1000	54.0
C_2F_5-	300	110	700	41.0
C_3F_7-	350	115	810	17.0

Table X

Comparative Yields of Alkfoxyl s-Triazines

R	Alkfoxyl Nitrile	Alkfoxyl Amidine
CF_3-	51%	-
C_2F_5-	41%	35%
C_3F_7-	17%	6%

Infrared Absorption Spectra of Alkfoxyl s-Triazines

The infra red spectra of the alkfoxyl s-triazines show a very characteristic strong band in the region 1565 cm^{-1} (6.4μ). The band was found at the same location in all three members of the series and is believed to be characteristic for the -C=N- in conjugated cyclic compounds.

Studies involving the conjugated cyclic structure, the -C=N- absorptions have been assigned as being within the range 1660-1480 cm^{-1}.[3] A strong absorption at or near 810 cm^{-1} (12.40$_4$) has been attributed to the ring structure of pyrimidine in studies of these compounds.[43] The triazine ring structure not being very different, shows characteristic absorption at this point too.

SUMMARY

The methods of preparation and some physical and chemical properties of six distinct classes of nitrogen containing fluorocarbon derivatives are presented. These compounds are the result of an investigation of a variety of reactions of the fluorocarbon nitriles and demonstrate, by their formation, some of the unique applications of this fluorocarbon derivative.

1. A series of alkfaryl amidines were prepared and some of their physical and chemical properties determined. These compounds are believed to have the following structure:

The specific compounds in which R_f equals: CF_{3-}, C_2F_{5-}, and C_3F_{7-} were prepared and characterized. These compounds represent the first instance of an uncatalyzed addition of ammonia to a nitrile to yield a free amidine. A possible reaction mechanism is proposed in an attempt to explain the apparent difference in amidine formation between the fluorocarbon and the organic nitriles.

2. A series of N-methyl and N, N-dimethyl substituted alkfaryl amidines were prepared and some of their physical properties determined.

These compounds are believed to have the following structures:

The specific compounds for R_f equals: CF_3-, C_2F_5-, and C_3F_7- were prepared and characterized.

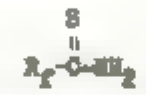
3. A series of metallic salts of alkforyl amidines were prepared. The salts prepared comprise the N-silver alkforyl amidines and the N-mercuric alkforyl amidines. The metallic salts show the apparent acidity of the alkforyl amidines in neutral solvents. The analysis of these compounds indicate that the alkforyl amidines act as monobasic acids.

4. A series of acid salts of the alkforyl amidines were prepared and characterized. These derivatives were formed with the inorganic, the organic and the fluorocarbon acids and indicate the apparent basicity of the alkforyl amidines under the condition of the reaction.

5. Acylation of the alkforyl amidines produced the N-acylated derivatives of the alkforyl amidines. These compounds, which hydrolyze to the primary amide and appear to be neutral substances, indicate that the imino nitrogen is the site of acylation. As such, they represent a departure in structure from most acylated organic amidines. These compounds are believed to have the following structure:

6. A reaction showing the rearrangement of the butforamidine under the influence of sodium hypobromite to the propfloryl bromide is presented. A possible path of the rearrangement is proposed.

7. A series of thioalkforesides were prepared and some of their properties determined. The preparation of these compounds was accomplished by two methods employing in the one case the alkforyl amidine and in the other case, the alkforyl nitrile. The compounds are believed to have the structure:



The compounds in which R_f equals: CF_3-, C_2F_5-, and C_3F_7-, were prepared and characterized.

8. The 1,3,5, tris(alkforyl) 2,4,6, s-triazines were prepared and characterized. These compounds were prepared by two independent syntheses using in the one case the alkforyl amidine and in the other case, the alkforyl nitrile. The compounds as prepared are believed to have the structure:

The compounds prepared and characterized were for R_f equals: CF_3-, C_2F_5-, and C_3F_7-. These compounds represent a departure from the conventional reactions of organic chemistry in that the trimerization of the alkforyl nitrile was accomplished without the use of a catalyst. The infrared spectra for these compounds is also presented.

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BIOGRAPHICAL NOTE

William Leo Reilly was born in Bayonne, New Jersey, on July 19, 1926.

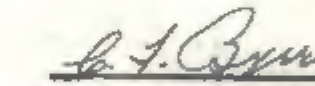
He attended West Virginia Wesleyan College from September, 1947 until June 1950, receiving the degree of Bachelor of Science. He entered Duquesne University in September, 1950 and received the degree of Master of Science in August, 1952. He then entered the University of Florida in September, 1952 and has been in attendance since that date.

The author belongs to Gamma Sigma Epsilon and Alpha Chi Sigma fraternities.

COMMITTEE REPORT

This dissertation was prepared under the direction of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Science and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 13, 1955



Dean, College of Arts and Science

Dean, Graduate School

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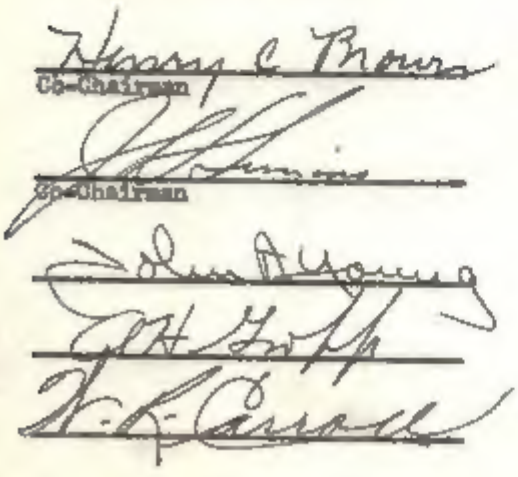

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